Chapter 2

Experimental methods

2.1 Growth of oxide thin films using molecular beam epitaxy

2.1.1 General considerations

Since its conception in the 1960s [1] [2] molecular beam epitaxy (MBE) has experienced a tremendous development [3]. Nowadays MBE includes the growth of metals, semiconductors, magnetic materials, nitrides, oxides and fluorides using solid and gaseous as well as metal-organic sources. MBE can best be described as a highly controlled deposition process. Epitaxial layers are grown in a ultrahigh vacuum (UHV) environment, by impinging thermal beams of molecules or atoms upon a heated substrate [4]. In the book of Braun [3] four major advantages of MBE as a tool for basic research and device production are summarized:

- MBE allows a very precise control of layer thickness and dopant incorporation down to the atomic scale.
- It facilitates analysis of growth processes such as surface migration and dopant incorporation.
- The UHV environment in the growth chamber allows the application of various in-situ measurement techniques to study the processes governing crystal growth. At the same time these measurements can be used to implement real-time feedback loops for growth control.
- Toxic chemicals are contained within the vacuum chamber.

In MBE, the composition of the grown material depends on the relative arrival rates of the constituents elements, which depend on the evaporation rates of the
various sources. In addition, a very important parameter for epitaxy is the misfit between the substrate and adsorbate lattice [5] [6].

There exist three different types of growth modes, namely: Frank van der Merwe (layer-by-layer) growth, the Stranski-Krastanov (island) growth characterized by an initial layer-by-layer mechanism followed by nucleation and growth of three dimensional crystallites, and finally the Volmer-Weber growth characterized by the growth of three dimensional clusters on the bare substrate [7].

2.1.2 MBE set-ups

For the sample growth we have employed two complementary ultra-high vacuum (UHV) set-ups.

The first one is a MBE system, primarily suited for studying the growth process and crystallographic structure of the films. A sketch of this system is shown in figure 2.1.

The system consists of three separate chambers: (1) The first chamber is a preparation chamber with facilities for electron-beam annealing of the substrates having a base pressure of about \(1 \times 10^{-10}\) mbar. (2) The second one is a growth chamber with a base pressure in the low \(10^{-10}\) mbar, equipped with a sample manipulator, evaporation sources made of alumina crucibles from which chromium and magnesium metals were evaporated, a stainless steel pipe to deliver the oxidizing agent to the sample, RHEED gun, a quadrupole mass-spectrometer for residual gas analysis and a quartz crystal microbalance to monitor the metal fluxes. The manipulator allows positioning and orientation of the crystal by adjustment of the x, y and z coordinates and of the polar and azimuthal angles. The sample temperature on the manipulator can be controlled between \(-140^\circ\)C and \(600^\circ\)C. The stainless steel pipe is connected with a buffer volume where the oxidizing agent was fed through a needle leak valve from an exterior bottle. The flux of the oxidizing particles at the substrate surface is proportional to the buffer volume pressure measured with a capacitance manometer. (3) There is finally, an analysis chamber which reaches the low \(10^{-11}\) mbar region and is equipped with a conventional X-ray source for XPS (Mg \(K_\alpha\) and Al \(K_\alpha\) radiations), a VG CLAM 2 hemispherical analyzer and a rear-view LEED apparatus with four grid optics.

The second ultra-high vacuum set-up is a high-resolution electron spectroscopy system dedicated for the determination of the electronic structure of the films. It has an attached deposition chamber for growing sample films \textit{in situ} under the
optimum conditions as determined in the MBE set-up. This preparation chamber has a base pressure in the low $10^{-10}$ mbar range system and it is equipped also with a sample manipulator, two effusion cells with manually controlled shutters used for chromium and magnesium metals, a stainless steel pipe to deliver the oxidizing gas connected with a buffer volume and a capacitance manometer, RHEED gun and a water cooled quartz crystal microbalance used to monitor the metal fluxes. Figure 2.2 is a schematic representation of the system geometry while growing the sample.

The manipulator has three degrees of freedom, i.e. $x$ and $z$ movement, and a rotation around the polar angle, used for the sample positioning, transportation into the system and to properly optimize the RHEED pattern. The sample temperature on the manipulator can be controlled between room temperature and $600^\circ C$. 

**Figure 2.1.** Schematic drawing of the MBE setup utilized for the chromium oxide growth study
The Cr effusion cell and the stainless steel gas pipe make an angle of 40° with the normal of the substrate surface. The oxidizing agent was fed from a bottle via a leak valve into the buffer volume and from here it was delivered via the nozzle to the substrate. The flux of oxidizing particles at the substrate surface is proportional to the buffer volume pressure, measured with the Baratron capacitance manometer. For measuring the metal fluxes, the quartz crystal microbalance was placed in the sample growth position, thus providing an accurate calibration.

At the small angles of incidence necessary to observe RHEED intensity oscillations, the samples grown on insulating substrates had a tendency to charge giving blurred RHEED patterns. To reduce the charging an additional low-energy electron flood gun was used. In order to improve the RHEED measurements we used also a beam shutter positioned before the RHEED screen with the role of reducing the intensity of the primary, undeflected electron beam and therefore providing a much lower background intensity.

In addition, the deposition chamber is provided with a cleaver for the UHV cleavage of bulk samples, and an annealing oven and a gas nozzle positioned at ≈ 5 cm from the oven in order to provide oxygen for substrate annealing.
The XPS part is equipped with a small spot (150-1000 µm) monochromatized Al $K_\alpha$ source and a hemispherical electron energy analyzer with multichannel detection system. The electrons were collected at a take-off angle of $55^\circ$ with respect to the surface normal of the samples. This system has also a rear-view LEED apparatus with four grid optics.

2.2 Analyzing techniques

The XPS part is equipped with a small spot (150-1000 µm) monochromatized Al $K_\alpha$ source and a hemispherical electron energy analyzer with multichannel detection system. The electrons were collected at a take-off angle of $55^\circ$ with respect to the surface normal of the samples. This system has also a rear-view LEED apparatus with four grid optics.

2.2 Analyzing techniques

2.2.1 In situ RHEED and LEED

In Reflection High Energy Electron Diffraction (RHEED) the primary electron beam of high energy (15 keV in our case) impinges upon the crystal surface at grazing incidence [3] [8]. The forward elastic scattering is very strong and the
streaked diffraction pattern observed on a fluorescent screen will be characteristic for the surface atomic arrangement. In Low Energy Electron Diffraction (LEED) an electron beam with a small convergence and variable energy (between 50 eV and 300 eV) impinges on the crystal surface at normal incidence and a spot-like diffraction pattern is observed on the fluorescent screen. Due to the geometry of the RHEED and LEED experiments, the reciprocal surface lattice is more easily recognized from a LEED pattern than from a RHEED one.

The high atomic scattering cross-sections for low-energy electrons makes LEED very surface sensitive. It is the electrostatic potential of the atoms which scatters these electrons. Although the mean free path of primary electrons in RHEED is much larger than in LEED, RHEED is also very surface sensitive because the incident angle is only a few degrees (0.5° to 3°), thus the penetration depth of the electron beam will be small. And since in MBE the molecular beams are incident nearly normal to the crystal surface, RHEED is geometrically more compatible than LEED to study the evolution of the surface structures during epitaxial growth.

When the intensity of the RHEED pattern is recorded as a function of time during sample growth, periodic oscillations can be obtained. It is generally accepted that these oscillations are a trademark of a two dimensional, Frank van der Merwe growth mode [9] [10]. For our experiments, during sample growth, the RHEED images were recorded in real time using a CCD camera and stored on a computer hard disk with a rate of one picture per second to allow subsequent analysis [11]. The incident angle of the RHEED beam corresponded to the first anti-Bragg position of the substrate, i.e. destructive interference of electrons scattered from surfaces separated by one monolayer in height.

2.2.2 In situ XPS

X-ray photoelectron spectroscopy (XPS) is accomplished by irradiating a sample with monoenergetic soft X-rays and analyzing the energy of the electrons emitted [12–15]. In our case, Al Kα X-rays with an energy of 1486.6 eV are used. These photons have limited penetrating power in a solid, of the order of 1-10 μm. They interact with atoms in this surface region by the photoelectric effect, causing electrons to be emitted. The electron escape depth is ranging from 2 to 20Å in the electron kinetic energy range of photoemission spectroscopy [16]. Therefore, special care has to be taken to avoid surface contamination or degradation. The kinetic energy of the emitted electrons is determined by the binding energy of the
shell from which the electron originates. The binding energy may be regarded as an
ionization energy of the atom for the particular shell involved. The electrons leaving
the sample are detected by an electron spectrometer according to their kinetic energy.

In our experiments, in addition to electronic structure determination, XPS was
also used to check for possible contaminations in the grown films and to determine
the stoichiometry of the chromium oxide samples.

### 2.2.3 Ex situ XRD and RBS/channelling

X-ray diffraction (XRD) is a very useful technique for structural characterization of
materials. Crystals, with regularly repeating structures, are capable of diffracting
radiation that has a wavelength similar to the interatomic distances [17]. In short,
the principle of this technique is: a collimated beam of X-rays impinges on the
sample and the intensity of the reflected beam is measured. When the scattering
angle and the interplanar spacing fulfill Bragg’s law, the reflected beams are in
phase and interfere constructively. At angles of incidence other than Bragg angle,
reflected beams are out of phase and destructive interference or cancellation occurs
[18].
In the experiments discussed in this thesis, XRD was used to identify the crystal structures of the grown chromium oxide samples. The measurements were performed *ex situ* using a Philips X'Pert materials research diffractometer (MRD) system in thin film configuration (ceramic X ray tube - line focus - giving CuKα radiation of 1.5418Å) with mirror and monochromator. Figure 2.3 shows a schematic representation of the geometry of the XRD measurement.

Rutherford backscattering spectrometry (RBS) is basically billiard-ball physics [7]. A beam of \( H^+ \) particles is directed at the sample at high enough energy (1.0 - 4.0 MeV) so that the particles scatter from the sample’s atomic nuclei in binary Coulomb collisions unscreened by the electron clouds (Rutherford scattering). The beam particles backscattered from the sample are detected and their energy is analyzed [19]. When the energy loss in the solid is not taken into account, the ratio between the energy of the particles before and after collision is determined only by the mass ratio of the particles and the geometry of the collision. Thus, atoms with different masses can be distinguished by their energy.

In the present work RBS measurements were used to identity the types of atoms involved in our samples, and they were used for structural analysis of the crystalline films based on the channelling effect [20]. Channelling occurs if a collimated beam impinges on a single-crystal target along a low-index direction. In that case the backscattering yield is reduced compared to the random incidence geometry because the probability of close collisions is diminished.

The RBS experiments were done *ex situ* in a high vacuum chamber with a base pressure of \( 5 \times 10^{-8} \) mbar. A 1 MeV \( H^+ \) beam was used and the backscattered beam was detected at two different angles: 105° and 135°.

### 2.2.4 *Ex situ* XAS

X-ray absorption spectroscopy (XAS) is a powerful technique for studying the local electronic structure. It measures the absorption of X-rays by sample, especially interesting at energies in the region of the absorption edges. A core electron is excited to an unoccupied state in the solid by the incident photon. Atoms give characteristic X-ray absorption spectra which arise from the various ionization and intershell transition that are possible [17]. The wavelengths at which the absorption edges occur depend on the relative separation of the atomic energy levels in the atoms which, in turn, depend on the atomic number.

XAS experiments were carried out at the Synchrotron Radiation Research Cen-
ter in Taiwan (SRRC - Taiwan) using the DRAGON monochromator [21]. The energy resolution of the monochromator at the Cr 2p edge was 184 meV. The energy scale was calibrated using NiO single crystal samples, for which the O 1s white line energy is known accurately from high energy electron energy loss spectroscopy experiments [22]. The spectra were recorded using the total electron yield (TEY) method [23].
References

[11] The data collection program and the analysis program were developed by T. Hibma, Dept. of Chemical Physics, University of Groningen.